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TECHNICAL REPORT

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MIGRATION OF SUBSTANCES FROM FLEXIBLE CONTAINERS FOR HEAT PROCESSED FOODS

by

M. Karel

G. N. Wogan

Massachusetts Institute of Technology

Division of Sponsored Research

Contract DA19-129-QM-2080(01 [illegible])

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Several methods for the determination of extractables in vegetable oils were evaluated, and applied to the correlation between extraction by oil and by n-heptane. The results indicate that the ratio of extractables obtained with oil to extractables obtained with n-heptane at 150°F varies with the nature of the material, and with the temperature of the oil. The results indicate also that the extractables from food packaging materials studied were composed primarily of either low molecular fractions of the base polymer, or of plasticizers contained in the materials.

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KEY WORDS	LINK A		LINK B		LINK C	
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Migration (substance)	8					
Solvent Extraction	8				7	
Adhesives	2		9		9	
Residues	2				9	
Flexible	0		0		0	
Films	1		9		9	
Laminated Plastics	1		9		9	
Containers	4		4			
Food	4		4			
Degradation			8			
Temperature					6	

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CONTRACT RESEARCH PROJECT REPORT
QUARTERMASTER FOOD AND CONTAINER INSTITUTE FOR THE ARMED FORCES
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SUMMARY

Thirteen different flexible packaging materials, potentially suitable for packaging of heat processed foods, were investigated with respect to the migration of their components during heat processing. The investigation had the following objectives: 1) determination of total amounts of substances migrating into food-simulating solvents; 2) general characterization of the chemical nature of the migrating substances; 3) evaluation of the safety of use of the materials, on the basis of standards established by federal regulations; and 4) investigation of methods for determination of extractables in vegetable oils, and correlation of amounts migrating into oils at different temperatures with amounts extracted by solvents. Results are presented on the total amounts of extractables obtained by exposure of the materials under heat-processing conditions to water, acetic acid solutions and n-heptane.

The effect of heat-sealing of the materials on their extractability was also determined, and results presented.

Several methods for the determination of extractables in vegetable oils were evaluated, and applied to the correlation between extraction by oil and by n-heptane. The results indicate that the ratio of extractables obtained with oil to extractables obtained with n-heptane at 150°F varies with the nature of the material, and with the temperature of the oil.

The results indicate also that the extractables from food packaging materials studied were composed primarily of either low molecular fractions of the base polymer, or of plasticizers contained in the materials.

I. Introduction

The present project is concerned with the migration of substances from various packaging materials, which may be used for packaging of heat-processed foods, into several food simulating solvents.

The specific objectives of the project included:

(1) Determination of the total amounts of substances migrating into the solvents under various conditions of processing.

(2) Collection of analytical data, allowing general characterization of the migrating substances.

(3) Assessment of the potential hazard of using the packaging materials under heat-processing conditions, on the basis of safety standards established by the Food and Drug Administration.

(4) Investigation of methods allowing direct determination of the migratory substances in vegetable oils, and the use of these methods to correlate amounts extracted by vegetable oil with those extracted by solvents, under various processing conditions.

II. Migration of Substances into Food-Simulating Solvents

A. Equipment and Procedures

1. Packaging Materials

Thirteen different materials which were of particular interest to the Food and Container Institute were selected for the study. They were obtained directly from the various manufacturers.

The complete details on the nature and source of each of the materials discussed in the present report have been submitted to the Project Officer, Mr. Joseph Szczebrowski, in a separate letter.

In some cases the manufacturers were able to supply some information on the extractability of the materials by food-simulating solvents. This information has been forwarded to the Project Officer, and does not form a part of the present report.

2. Extraction of Materials with Water

a. Heat processing retort. A vertical retort was adapted for extraction studies at high temperatures. The retort is equipped with steam as a source of heat, with cold water for the cooling cycle and with compressed air for cooling under superimposed air pressure. The retort was found to allow the conduction of controlled extraction studies up to temperatures of 300°F. A schematic diagram of this equipment has been presented in a previous report (1).

b. Extraction cells. Two types of cells were constructed for the extraction studies. The dimensions and materials of construction for the two types of cells were presented in a previous report (1).

The single chamber cell was identical to that reported by Maturi et al. (2). Subsequently a four-chamber cell was constructed in order to conduct tests in quadruplicate with a minimum of labor and equipment. The volume to area ratios in both types of cells

are identical and are 2 ml/in^2. All chambers were subjected to preliminary tests to assure that they were free of leaks.

The teflon gaskets of all extraction cells were subsequently modified to conform with the type of gasket used in commercial cells (Scientific Products, Evanston, Illinois). This type of gasket was found to improve cell performance in the following respects: (1) improved leak-tightness; (2) improved sample area control.

c. Procedures for extraction of unsupported films with water. The water used in all extraction procedures was distilled water subjected to an additional demineralization procedure immediately prior to use. The demineralizer used was equipped with a gage capable of detecting 0.02 ppm of NaCl.

Blank residue determinations were made on this water and the total residue was found to be 1.25 mg per liter. Of this total residue 0.88 mg per liter were found to be chloroform-soluble.

Blank residue determinations were also made on the extraction cells. This was accomplished by exposing 200 ml of water in a chamber of the extraction cell to a temperature of 212°F for two hours and subsequent determinations of the residue in this water. The blank residues were between 0.30 and 0.37 mg per cell. It was also determined that all of this residue was due to components removed from the stainless steel walls of the cells. Since these walls are covered with the test materials during actual runs, it

was felt that the cell blank did not have to be subtracted from the experimentally determined residue amounts.

The film samples were cut to fit under the inner seal of the teflon gaskets. The cells were loaded in the arrangement shown in a previous report (1). The bolts were tightened with a small wrench. The cells were then washed in a Typhoon Model Heinicke Lab-Glassware Washer using tap water at 190-200°F for one minute, followed by a cold distilled water rinse for one-half minute. The cells were allowed to drain for a few minutes.

A measured volume of water was poured into each chamber allowing enough volume for the expansion of water so that on heating the ratio of water volume to surface area of film would be approximately 2 ml/in^2. The cells were then covered with aluminum foil and placed in the cell container in the retort. After closing the retort, the steam was turned on. After blowing the air out, the steam pressure was increased to the required value and held there for the desired extraction time. At the end of the heating cycle, the air line was opened to supply a controlled, superimposed air pressure and the steam was turned off. Cold water was turned on to cool the cells. After cooling, the cells were transferred to a bench and the solvent was removed from each chamber by a siphon connected to a collection flask which was evacuated by aspiration. Processing at atmospheric pressure was accomplished by exposure of cells to free flowing steam.

The volume of the solvent was measured and then concentrated to about 30 cc by evaporation. It was then transferred to a pre-weighed platinum dish and evaporated further over a low-temperature, electric heating plate. The platinum dishes were then dried for 30 minutes in an oven at 212°F. The platinum dishes were cooled in a desiccator and weighed. The total extractable residue was calculated as mg per square inch.

Chloroform-soluble residue was determined as follows. To the total residue were added 50 ml of chloroform (reagent grade, having a consistently low blank). The chloroform was carefully warmed to approximately 110°F and then filtered into a tared platinum dish. It was then evaporated over a steam bath and finally dried in an oven at 212°F, cooled in a desiccator and weighed. The amount of chloroform-soluble residue was calculated as mg per square inch.

d. Procedures for extraction of laminations. Preliminary experiments on laminations have indicated that the procedures used for unsupported films were not satisfactory for use with laminations. In this case significant water losses (up to 50%) were encountered which resulted in excessive variation in the results. Although the exact mechanism is not known, it is believed that the problem arises from the fact that laminates become distorted during processing and push the water out of the chamber.

The difficulties were overcome by the use of one of the following modifications:

(1) Samples were cemented with adhesive to the stainless steel plates of the extraction cells.

(2) Samples were made into pouches, filled with distilled water, the pouches sealed in water-filled cans and processed in the retort at the appropriate times and temperatures.

(3) Solvent volume to sample area ratio was increased by elimination of intermediate plates in the four-chamber cell. The larger solvent volume resulted in making the solvent losses less significant in proportion to total volume recovered.

Each of the above methods appeared to allow a satisfactory extraction and the results of extractions using the three methods gave comparable results.

e. Checks on residue recovery. It was thought desirable to determine whether solubility in water was a limiting factor in the residue recovery. This aspect was particularly important because of the following factors:

(1) The solvent volume to sample area ratio used in the extraction procedure (2 ml/in^2) is less than that obtainable in normal commercial packages.

(2) The procedures involved evaporation of part of the solvent in glass dishes, with subsequent transfer of the remaining solvent to tared platinum dishes from which the remainder of the

solvent is evaporated. Precipitation of the residue in the glass dishes due to a limiting solubility would result in decreased values of residue as determined by the present procedures, which are based on federal regulations (3).

The procedure was checked as follows:

(1) Extractions were performed at volume to area ratios of 2 ml/in^2, 2.5 ml/in^2 and 8 ml/in^2. The results are presented in Table I.

(2) Solvent was evaporated by using the normal evaporation procedure using glass dishes and subsequent transfer to platinum dishes, as well as by performing all evaporation from the tared platinum dishes. The results are presented in Table II.

It is evident from the results presented in the two tables that neither the volume to area ratios nor the drying procedures were a limiting factor in the residue recovery for the film tested (Code: L3).

A further check of the standard recovery procedure used in the present study (based on federal specifications (3)) was made by extracting samples of material L4 with distilled water at 267°F in accordance with procedures outlined previously. The evaporation of the water was conducted according to the following procedures:

(1) Standard recovery procedure.

(2) Evaporation to constant weight at atmospheric pressure in a desiccator over a mixture of anhydrous calcium chloride and calcium sulfate. The residues obtained in this manner were weighed, and then dried for one-half hour at 100°C and reweighed after cooling in a desiccator. The following results were obtained:

Standard recovery procedure: Sample 1: 4.2 mg residue per 100 square inches

Sample 2: 4.46 mg residue per 100 square inches

Desiccator recovery: Sample 3: 7.15 mg residue per 100 square inches

Sample 4: 8.08 mg residue per 100 square inches

After one-half hour heating at 100°C:

Sample 3: 6.46 mg residue per 100 square inches

Sample 4: 7.15 mg residue per 100 square inches.

These results indicate the possibility that some volatile components may be lost during the standard evaporation procedures. Because of the low levels of total residues involved, however, this conclusion must be considered tentative.

f. Determination of come up time. In order to assure the reproducibility of the results, heating and cooling curves for the solvent in the center of the cell chamber, or pouch, were obtained at several retort temperatures. The heating and cooling curves are presented in Figures 1, 2, 3 and 4.

The temperatures were determined by placing copper constantan thermocouples in the centers of the cell chambers or pouches and recording the temperatures with a Leeds and Northrup portable potentiometer (Cat. No. 8692).

3. Extraction with 0.4% Acetic Acid Solution

a. Solvent. A 0.4% acetic acid solution was prepared using reagent grade acetic acid (Mallinckrodt) and distilled water. The pH of the solution was checked before and after extraction and found to be 3.2. The solution was tested for residue content and gave a blank of 1 mg/liter.

b. Extraction procedures. Unsupported films were extracted in extraction cells, laminated materials were fabricated into pouches and filled with the extracting solution. The procedures were identical to those reported for extraction with distilled water.

4. Extraction with n-Heptane

a. Solvent. 99% pure n-heptane (M.I.T., Office of Laboratory Supplies) was used as the extracting solvent. The boiling point and the infra-red absorption spectrum of this solvent were identical to that of "Spectranalyzed Analytical Reagent" (Fisher) n-heptane. The blank residues were in the range of 0.6 to 1.0 mg per 200 ml.

b. Procedures for extraction in cells. Four-chambered cells described in a previous report (1) and modified as described previously were used. The cells were washed, as described previously,

preheated to 150°F and the solvent at 150°F introduced into each chamber through a glass funnel fitted with tygon tubing reaching to the bottom of the chamber. This arrangement prevented the washing of warm solvent over the film during filling of the cells. Contact with warm solvent caused buckling of the films and loss of solvent through overflow and seepage between the film samples and the steel plates.

Blank determinations on the empty cell were high and very variable. Since most of the area of the cell, the stainless steel surface, is not exposed to the solvent during the actual tests, a cell blank was determined in the following manner: fifty square inches of the film having the lowest amount of extractables per square inch was cut into one-inch squares and refluxed in heptane for 2 hours at 150°F. This procedure extracts about 60% of the extractables removed in a cell extraction. Therefore, the residue determined by the cell method minus the residue determined by the reflux method (divided by 0.6) equals the cell blank. The average cell blank was 2.9 mg per cell chamber.

c. Extraction by refluxing. In addition to extraction in cells some samples were also extracted by refluxing of films cut into small samples in n-heptane for 2 hours at 150°F. In this procedure the extraction was proceeding from both sides of the samples.

d. Extraction in pouches. This procedure is the same as that described in section II.A.2.d.(2).

e. Recovery procedures. The determination of the amount of extractables as detailed by federal regulations (3) was followed, except that the preliminary evaporation of the solvent was conducted by evaporation from platinum dishes on a steam bath.

f. Infrared analysis of n-heptane residues. Infrared analyses of the n-heptane residues of the film extractables were made in carbon tetrachloride against air, using a Beckman IR-5 Infrared Spectrophotometer. The samples were dissolved in a minimum amount of solvent; therefore, quantitative comparisons could not be made between the intensity of particular functional group absorbances in different films. One heptane residue was insoluble in any of the common solvents; its infrared spectrum was determined in nujol against air.

5. Effect of Heat Sealing

a. Extraction with water. The materials tested were heat-sealed over approximately one-half of their surface area. The materials were then extracted in the form of pouches as described previously. The condition of heat sealing for each of the films tested are presented in the section on results. The heat sealer used was an automatically controlled air-operated jaw sealer (Robot-Pack-Rite Machines).

b. Extraction with 0.4% acetic acid solution. The extraction procedure was carried out exactly as described for the water extraction of heat sealed films. The extracting solvent was 0.4% acetic acid, pH 3.2.

c. Extraction with n-heptane. The materials were formed into pouches which were filled with cold heptane, and then heated for 2 hours at 150°F. The other details of the extraction with heptane were the same as described in the preceding section.

B. Results

1. Extraction with Distilled Water

All unsupported films (U1-U7) were extracted for 2 hours at their maximum use temperature using standard procedures referred to hereafter as Method I and described in section II.A.2.c. of this report. The quadruplicate determinations in the gasketed ASTM cell were satisfactory. The results are presented in Table III as mg/in^2 of extractables and as concentration of residue in the solvent in parts per million.

The chloroform soluble portions of the residue have not been discussed in this report since the total residues are considerably lower than the acceptability limits set by the Food and Drug Administration.

The laminations (L1-L6) were extracted using the modifications described previously. These modifications were as follows:

Method II: As Method I, but samples held in place by cementing to stainless steel plates of the cell.

Method III: Samples extracted in pouches had a sample area of 28 in^2 and a solvent volume to sample area ratio of 2.5 ml/in^2.

Method IV: As Method I, but solvent volume to sample surface ratio of 8 ml/in^2.

The extraction results obtained by all four methods agreed quite well; however, only the results of Methods I and II are presented in Table III.

All results present net residues, since the water blanks were subtracted from the total residue weight. The cell blanks on the loaded cells were assumed to be negligible compared to the obtained residue weights.

It is apparent from these results that all of the thirteen materials tested showed extractable amounts which were lower than the maximum amounts allowed by federal regulations (3).

2. Extraction with 0.4% Acetic Acid Solution

The results of extraction of various materials with 0.4% acetic acid solutions (pH 3.2) are presented in Tables IV and V. It was impossible to obtain a satisfactory blank value for empty cell, since the acetic acid solution extracted significant but variable amounts from stainless steel. On the other hand in actual

operation the stainless steel surfaces are not exposed to the solvent. It was assumed, therefore, that extraction from surfaces other than the films tested was negligible, and that the residues determined experimentally required no blank correction other than the blank of the solution itself.

The results show that acetic acid solutions at pH 3.2 extract amounts comparable to extractives obtained with distilled water. (The actual ratios of the extractives obtained with these solvents for individual materials varied from 0.5 to 5.)

3. Extraction with n-Heptane

The complete results of extraction with n-heptane at 150°F are presented in Table VI. These results show that several of the materials give residues in excess of amounts acceptable under federal regulations. Seven of the thirteen materials tested showed levels below the maximum acceptable under federal regulations and show promise as acceptable materials for packaging of heat-processed fatty foods.

The heptane residues were further analyzed spectrophotometrically to obtain information on their chemical nature.

The ultraviolet absorption of these residues dissolved in cyclohexane or heptane and analyzed on a double beam instrument (Beckman Model DB) was non-specific and not useful for analytical purposes.

The infrared analyses as described in the section under procedures gave more positive results which are presented in Table VII.

The residues from U1 appear to be primarily partially oxidized hydrocarbons. The spectra of U2, U3, and U4 are all quite similar and suggest the possibility of phthalate residues. The spectrum of U5 is also suggestive of a phthalate ester and gave a more complete spectrum because of its greater solubility in carbon tetrachloride. The spectra of U6, U7, and L1 suggest long chain hydrocarbons which have been partially oxidized. The L2 and L3 residues appear to be aryl esters, probably phthalate. The spectrum of L4 in nujol is also suggestive of an aryl ester. L5 and L6 appear to be partially oxidized hydrocarbons.

4. Effect of Heat Sealing

The results of extractions of the heat sealed materials in the form of pouches with water, acetic acid and n-heptane are presented in Tables VIII to X. The area exposed to heat sealing was greatly in excess of that expected in normal usage.

The solvents tended to remove more extractables from the heat sealed films. In some cases the water extracted 3 times as much from heat sealed films. In general the acetic acid extracted 8 to 12 times as much from the materials after heat sealing. n-Heptane extracted only slightly more after heat sealing.

5. Evaluation of Acceptability

Acceptability of the materials tested is presented in Tables XI and XII. On the basis of the present F.D.A. regulations materials U5, L2 and L3 are unacceptable for high temperature processing of fatty foods as judged on the basis of mg extractables/ in^2; films U2, U5, U6, L2, L3 and L4 are unacceptable for the same type of processing as judged on the basis of ppm at 2.5 ml solvent/ in^2.

III. Correlation of Amounts of Extractives Obtained from n-Heptane at 150°F with Those Obtained by Extraction with Oil at Several Heat Processing Temperatures

A. Introduction

In addition to the standard solvent extractions of the materials listed previously, an attempt has been made to determine the validity of using a fixed ratio between the amount of the heptane extractables of a specific material at 150°F and the amount of extractables obtained with oil at higher temperatures. The present estimation of acceptability of materials for high temperature heat processing of fatty foods (3) is based on the assumption that extraction with n-heptane at 150°F for 2 hours results in amounts of residue five times larger than those obtained by extraction for 2 hours with oil at 250°F. Since the conditions under which this assumption holds do not seem to have been thoroughly investigated,

it was considered desirable to undertake further investigations in this direction.

B. Experimental Approach

Several analytical procedures were tested for their suitability for the determination of total extractables in vegetable oil. In each of these procedures, the heptane and oil extracts of the material under investigation were obtained in the same way. Unsupported films were extracted by the reflux method described in section II.A.4.c of this report. Laminated materials were extracted in pouches as described in section II.A. 2.d.(2).

For most of the oil extractions the vegetable oil used was olive oil; in a few instances triolein was used for reasons which will be discussed under each analytical method for which it was used.

A total of eight analytical methods have been tried in this work in which oil extracts were compared to heptane extracts and to oil to which heptane extracts had been added.

C. Results of the Evaluation of the Problem by Various Analytical Procedures

1. Ultraviolet Analysis

Materials U2 and U5 were refluxed for 2 hours in heptane or olive oil. The heptane extract was dried, weighed, redissolved in heptane and accurately diluted to a known concentration. The

oil containing the oil extract was accurately diluted with heptane so that in the final solution the oil extract was thought to be present in roughly the same concentration as the heptane extracts in their corresponding solutions. Heated oil samples containing no extract were diluted to the same degree and used as blanks. The samples were scanned in the region of the ultraviolet spectrum; it was hoped that the samples might absorb at a wavelength where absorption due to oil was minimal. The analyses were unsuccessful because the amounts of residues were below the limit of detection of the analytical method. Apparently the blank was too high to detect a difference between the blank and the sample.

In a further refinement of the ultraviolet analysis of an oil extract (4) a sample of olive oil containing the oil extract of L3 was extracted with methanol, saponified, filtered and its absorbance in acid measured at 275 mμ and 250 mμ. Even after partially purifying the samples by methanol extraction, the blank readings were too high and nearly equalled the absorption of the actual samples.

2. Chromatographic Analysis

a. Column chromatography. This method is based on the work of Phillips and Bluestein (5) who used it to determine the presence of hydrocarbons in food. The foods in question were extracted with a solvent and chromatographed directly on alumina. The method is based on the assumption that triglycerides and esters are held on the alumina column and hydrocarbons are eluted.

In experiments conducted in this laboratory, samples of heated olive oil used as blanks, heptane residues, and oil containing extracts were chromatographed with n-heptane on 9 x 170 mm columns packed with 48-100 mesh, Alcoa, F-1, alumina, activated for 1 hour at 1000°F. The columns were prewashed, before use, with solvent until no residue was detectable in the eluent.

Maximum sample size was 400 mg. The operating characteristics of the columns were obtained by plotting elution curves as total volume of solvent against the weight of residue in each 10-ml portion of the solvent.

The columns retained about 95% of the olive oil samples; a non-polar fraction (about 5% of the sample) was eluted with 250 cc of solvent. If the columns were pretreated by passing a heptane extractable residue of L1 through them, subsequent heptane extractable residues of L1 could be recovered without measurable losses.

The oil and residue samples were so heterogeneous that both were eluted as multiple fractions. The non-polar oil fraction and the heptane residues were partially separated, the latter being eluted faster. Heptane residues dissolved in oil and actual oil extracts behaved similarly; however, variability was great and it would seem that this procedure is best used as a concentration procedure for further analysis. The non-polar oil fraction and the extract should be collected together; 95% of the oil would be left on the column.

Triolein was used as the extracting oil in an attempt to minimize the variability of the elution pattern of the oil. The results indicated, however, that the variability with the triglyceride was comparable to that obtained with olive oil.

b. Thin layer chromatography. The total eluate from the columns as described above was chromatographed with n-heptane on silica gel G (E. Merck A.G. Darmstadt, Germany). The chromatograms were sprayed with sulfuric acid to develop the spots.

The chromatographic patterns agreed very well with the elution curves of the columns. The chromatographic pattern of the heptane residues of plasticized films using chloroform as the eluent was very different from that of pure oil samples; however, in oil extracts of these same films no extracts were visualized by sulfuric acid development. This is probably due to the low concentration of residue in the oil which limited the sample size that could be put on the plate. The amount of oil, which would have to be placed on the plate in order to detect the residue in the oil, would have resulted in flooding the chromatographic plate. It appears, therefore, that further work in the improvement of this technique is necessary, but this work is outside the scope of the present project.

3. Gravimetric Difference Method

The procedure used in this semi-quantitative method was as follows:

Materials formed into pouches were extracted twice with n-heptane to determine the limit of extractability of the material. It was observed that additional extractions yielded little additional residue. Samples of the same material were then extracted with olive oil at 250°F, washed with 3-5 cc portions of cold heptane to remove excess oil and then extracted with n-heptane at 150°F for 2 hours.

Extractives removed from fresh samples by 3-5 cc portions of cold heptane were determined and added to the values obtained by heptane extraction on samples undergoing a previous olive oil extraction. A rough estimate of the amount extracted by olive oil at 250°F was obtained by difference as follows:

Amount extracted by oil = (amount extracted by double heptane extraction) - (amount extracted by heptane extraction following an oil extraction + amount extractable by washing with cold heptane)

The results of these tests are shown in Table XIII. These results should be considered as only semi-quantitative, but they indicate that the ratio of n-heptane extractables to oil extractables may differ significantly from the assumed value of 5:1.

4. Gravimetric Determination of Non-saponifiables

The procedure used for this analysis was the official method of the AOAC (6).

About 2 gm of olive oil (or triolein) containing the oil extract was refluxed with alcoholic KOH. The warm soap solution was ether extracted, washed and evaporated to dryness. The resulting residues were determined gravimetrically. A similar problem was encountered here as was found in the ultraviolet analysis; the high blank for the oil precluded accurate analysis of the residue in the oil extract, since after extraction the oil used had only a slightly higher non-saponifiable content than the oil by itself.

This problem was partially overcome by extracting a series of pouches of L6 with the same portion of triolein. Triolein was used because of a much lower non-saponifiable content. Assuming that the limits of solubility of residue in oil were not exceeded, this method could be used to increase the concentration of residue in the triglyceride. Ten 25-in^2 pouches were extracted successively for 2 hours with a single 25-ml portion of oil. At each transfer about 1.8 ml of oil was lost. The final pouch yielded 7 ml of oil containing 14.2 mg of non-saponifiable residue (corrected for the oil blank on triolein heated for 20 hours). Assuming that the final sample was representative, the first extraction (pouch #1) would have contained one-tenth as much residue or 0.2 mg/ml. Each additional extraction would take out an incremental amount (+ .2 mg/ml). Based on this assumption, it was calculated that 22 mg of residue was lost in the 18 ml of oil

which were lost; therefore, the total extract was 22 mg plus 14.2 mg or 36.2 mg for 250 in^2 (0.145 mg/in^2).

A sample of the heptane extract could not be saponified for comparison because it was not soluble in the alcoholic KOH; therefore the weight of the heptane residue, assumed to contain no saponifiable matter, (0.281 mg/in^2) was compared directly with the non-saponifiable weight of the oil extract (0.145 mg/in^2). The ratio is 1.94 compared to 2.86 for the gravimetric difference method.

5. Infrared Analysis of Extracted Films

This analysis is based on a procedure worked out by Eich (7) using the infrared absorption of the film at 5.80 microns as a measure of the degree of extraction of plasticized films. The method assumes that 100% extraction of a film is equal to the difference in extinction between a fresh sample of film at 5.80 microns and a sample of film which has been extracted with ether for 5 hours. The method further assumes that the oil used in extraction can be removed from the film after extraction so that it does not interfere with the absorption at 5.80 microns due to the plasticizer; furthermore it is assumed that the change in absorption of the extracted film at 5.80 microns is linear with the fraction of plasticizer removed.

The film used in this project contained too much plasticizer to make use of Eich's method. The change in absorbance

as an indication of 100% removal of plasticizer was too great to be measured; therefore, the absorbance of heptane extracted films was plotted against mg of residue from the heptane extractions for different lengths of time. It has been assumed that the heptane and oil extract the same type of material and that absorption at 5.75 microns, the absorption maximum for the plasticizer, is an accurate measure of extraction. The per cent plasticizer removed by olive oil at 250°F was found from the standard curve.

The following data have been obtained on material U5:

Extraction	Residue in mg	Absorbance
1 hour heptane extraction	2.16	.130
2 hour heptane extraction	3.05	.053
4 hour heptane extraction	4.05	.040
2 hour oil extraction		.160

From a plot of mg residue vs. absorbance extrapolated to an absorbance of 0.16 the oil extracted residue is 2.13 mg; the ratio of heptane extractables to oil extractables is 1.43 compared to 1.20 for L3, a similar film.

6. Nephelometric Analysis

The work of Johnson and Critchfield (8) is the basis of work done in this laboratory. Their work was aimed at determining the per cent of extractables which could be obtained from their materials at or below an extraction temperature of 50°C in hexane;

these extractables were termed the Low Molecular Weight Fraction. A certain per cent of this fraction can be precipitated in an ethyl-isopropyl alcohol mixture and analyzed turbidimetrically.

The analysis done in this laboratory was aimed at a comparison of heptane extraction at 150°F with oil extraction at 250°F, and higher temperatures.

Standard curves shown in Figures 5 and 6 were obtained by mixing serial dilutions of a 2 hour heptane extraction of the material in question at 150°F with an equal volume of olive oil. The final solutions were mixed with ethyl and isopropyl alcohols and analyzed turbidimetrically using a Coleman Model 7 Nephelometer. The oil extracts of the materials in olive oil were mixed with an equal volume of heptane. The residues were precipitated with alcohol as described above. The amount of residue in oil was estimated from the standard curve for the material in question. The results, as well as the actual mg of heptane extractables for the same materials, are presented below.

Material	Temperature of oil extraction	Estimate of mg of oil extractables/in^2	Mg heptane extractables/in^2 at 150°F
L6	250°F	0.0677	0.2142
L6	275	0.136	0.2142
L6	285	0.900	0.2142
L6	300	4.600	0.2142
L1	212	1.239	1.184
L5	212	0.305	0.061

The ratio of heptane extractables at 150°F to oil extractables at 250°F was found to be 3.16, at 275°F the ratio was 1.58, at 285°F it was 0.238, and at 300°F it was 0.0466.

D. Conclusion

It appears from these results that the ratio of heptane extractables at 150°F to oil extractables varies from material to material and is also a function of oil extraction temperature. A summary of results obtained by various procedures is presented in the following:

Ratio of Heptane Extractables at 150°F to Oil Extractables at Specified Temperatures

Method of analysis	Material	Ratio of heptane extractables at 150°F to oil extractables at specified temperature
Gravimetric difference method	L2	1.08 (250°F)
	L3	1.20 (250°F)
	L4	2.32 (250°F)
	L6	2.86 (250°F)
Non-saponifiables	L6	1.94 (250°F)
Infrared	L5	1.43 (250°F)
Turbidimetric	L1	.956 (212°F)
	L5	.200 (212°F)
	L6	3.16 (250°F)
	L6	1.58 (275°F)
	L6	.238 (285°F)
	L6	.0466 (300°F)

IV. Suggestions for Future Research

A. Introduction

The results obtained in the present investigation have revealed that there are several interesting problems which warrant further investigation. Discussions with the Project Officer, Mr. J. W. Szczeblowski, have further confirmed the investigators' opinion that these problems are of importance to the packaging program of the Food and Container Institute.

B. Plan of Approach

The proposed investigation should include the study of the following problems:

1. Further Development of Methods for the Accurate Determination of Extractives from Packaging Materials in Oils and in Pure Triglycerides

Several methods show potential for further development. The methods to be studied include:

a. Column chromatography

b. Quantitative infrared spectrophotometry

c. Thin layer chromatography

d. Nephelometry

2. Establishing Reliable Relationships Between Extractability of Packaging Materials by Oils and Triglycerides

As soon as reliable methods for the determination of extractives in oils and/or triglycerides are developed, they

could be applied to the determination of the following relationships:

a. Quantitative relationship between amounts extracted from different materials by oils and/or triglycerides at various temperatures, and the amounts extracted by n-heptane at 150°F.

b. Quantitative relationship between amounts extracted by n-heptane at 150°F, and the amounts extracted by aqueous emulsions of oils and/or triglycerides at various temperatures. The concentrations of the oil in the emulsions should be maintained at several levels representative of several fat-containing foods.

3. Evaluation of the Possible Off-Flavor Significance of the Volatile and Non-Volatile Components Extracted from Packaging Materials During Heat Processing

a. The volatile components extracted by several solvents from different packaging materials could be estimated by trapping the volatiles during evaporation of the solvent in a series of graded-temperature cold traps and separating the condensables in each trap by gas chromatography. Further characterization of the volatiles would depend on the quantities obtained and on their chemical and physical properties.

The present procedures for the determination of total residues from packaging materials include the evaporation of solvent at high temperatures, and may result in considerable losses of volatile components. Preliminary experiments have in fact established such losses actually occur.

b. The off-flavor contribution of the volatile and non-volatile residues shoul be determined by organoleptic tests on foods processed in the packaging materials, and on foods or model systems to which residues obtained by water extraction have been added.

In cases where the residues are above the levels allowed by federal regulations, the organoleptic evaluation would consist of smelling only.

4. Determination of Total Residues in Several Food-Simulating Solvents for Additional Packaging Materials

The extraction procedures developed in the present investigation could be applied to the determination of extractives from additional heat-resistant packaging materials. Particular emphasis should be placed on newly developed plastics and laminates showing promise for military applications.

5. Chemical Characterization of the Residues

Further investigation should be made of the chemical nature of the extracted components. This investigation would aid in establishing the off-flavor and pharmacological significance of the residues.

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Table I

Comparison of Water Extractables from Material L3 Extracted in Pouches and in the ASTM FDA Proposed Extraction Cell at Two Different Volume to Area Ratios (Conditions were 0.5 hour at 252°F.)

Solvent volume/sample area (ml/in^2)	Extractables (mg/in^2)
2/1 (using ASTM cell)	0.0426
	0.0405
	0.0492
	0.0501
8/1 (using ASTM cell)	0.0425
2.5/1 (pouches)	0.0525
	0.0535
	0.0610
	0.0610

Table II

Comparison of Residue Recoveries Using Different Methods of Solvent Evaporation (Material L3, 250°F, 0.5 hour)

Total residue (mg/in^2)	
Standard method	Direct evaporation from the platinum dish
0.0426	0.0492
0.0405	0.0501

Table III

Results of Extraction with Distilled Water for 2 Hours at Maximum Use Temperature

Material	Extraction temperature (°F)	Extractables (mg/in^2) Average	Range	ppm in solvent at 2 ml/in^2
U1	292	.0294	±.0021	15.5
U2	276	.0256	±.0032	13.5
U3	292	.0219	±.0012	11.5
U4	292	.0396	±.0016	20.8
U5	276	.0349	±.0014	18.4
U6	212	.0095	±.0005	5.00
U7	212	.0077	±.0012	4.00
L1	212	.0102	±.0008	6.00
L2*	267	.0386	±.0038	22.7
L3	276	.0546	±.0052	32.1
L4*	267	.0798	±.0064	47.0
L5	212	.0125	±.0018	7.40
L6*	289	.0486	±.0051	28.6

*These films were extracted by Method II as presented in section II.B. of this report.

Table IV

Results of Extraction with 0.4% Acetic Acid (pH 3.20) for 2 Hours at Maximum Use Temperature

Film	Extraction temperature (°F)	Extractables (mg/in^2) Average	Range	ppm in solvent at 2 ml/in^2
U1	292	.0216	±.0021	12.0
U2	276	.0183	±.0019	11.0
U3	292	.0457	±.0100	27.0
U4	292	.0348	±.0004	20.0
U5	276	.0367	±.0033	22.0
U6	212	.0142	±.0019	8.00
U7	212	.0182	±.0035	11.0

Table V

Results of Extraction with 0.4% Acetic Acid (pH 3.20) for 2 Hours at Maximum Use Temperature

Film	Extraction temperature (°F)	Extractables (mg/in^2) Average	Range	ppm in solvent at 2.5 ml/in^2
L1	212	.0044	±.0004	1.76
L2	267	.0269	±.0027	10.8
L3	276	.0301	±.0026	12.0
L4	267	.0126	±.0020	5.04
L5	212	.0050	±.0003	2.00
L6	289	.0536	±.0079	21.4

Table VI

Results of Extraction with n-Heptane for 2 Hours at 150°F

Film	Extractables (mg/in^2) Average	Range	ppm in solvent at 2 ml/in^2	Corrected values* Extractive	ppm
U1	.068	.016	34.0	.014	6.80
U2	.447	.029	263	.089	52.6
U3	.025	.022	14.7	.005	2.94
U4	.007	.010	4.10	.001	.820
U5	5.52	.185	3250	1.10	650
U6	.634	.038	373	.127	74.6
U7	.320	.032	188	.064	37.6
L1	.355	.019	209	.075	42.0
L2	5.69	.171	3350	1.14	670
L3	5.30	.023	3120	1.06	624
L4	.949	.048	559	.190	112
L5	.161	.019	94.7	.032	18.9
L6	.210	.036	124	.042	24.8

* presented in amendment published in Federal Register February 10, 1962, 27F.R., 1252, Paragraph 121.2514, Section e, Subparagraph 5.

Table VII

Infrared Analysis of Heptane Extractables of Flexible Films

Film	Wavelength of absorption maxima	Probable function grouping
U1	3.42 (w)*	CH_2 - stretching
	3.51 (w)	CH_2 - stretching
	5.77 (m)	C = O stretching
	6.81 (w)	CH_2 bending
	10.72 (w)	unidentified
U2	3.41 (w)	CH_2 stretching
	3.49 (w)	CH_2 stretching
	5.78 (w)	C = O stretching (aryl ester)
	6.80 (w)	C = C stretching of benzene ring
U3	3.41 (m)	CH_2 stretching
	3.50 (m)	CH_2 stretching
	5.77 (m)	C = O stretching (aryl ester - tentative)
	6.85 (w)	C = C stretching of benzene ring
	7.25-7.38 (w)	unidentified
	10.72 (w)	unidentified
U4	3.41 (m)	CH_2 stretching
	3.50 (m)	CH_2 stretching
	5.77 (m)	C = O stretching (aryl ester - tentative)
	6.85 (w)	C = C stretching of benzene ring
	7.25-7.40 (w)	unidentified
	8.50 (m)	C - O - stretching (polyester)
	10.72 (w)	unidentified
U5	2.32 (w)	? water
	2.9 (w)	? water
	3.41 (s)	CH_2 stretching
	3.50 (s)	CH_2 stretching
	5.77 (s)	C = O stretching (aryl ester - tentative)
	6.85 (m)	C = C stretching of benzene ring
	7.05 (w)	C = C CH bending
	7.25-7.40 (m)	unidentified
	8.15 (s)	unidentified
	8.50 (s)	C - O - stretching (poly esters)
	8.75 (s)	C - O stretching (aromatic esters)
	9.40 (m)	? benzene ring substitution
	9.60 (m)	unidentified
	9.92 (s)	unidentified
	10.27 (m)	? benzene ring substitution

Table VII (cont'd)

Film	Wavelength of absorption maxima	Probable function grouping
U6	3.42 (m)	CH_2 stretching
	3.51 (m)	CH_2 stretching
	5.78 (m)	C = O stretching
	6.36 (w)	CH_2 or CH_3 bending
	7.05 (w)	unidentified
	7.25 (w)	CH_2 or CH_3 vibration
U7	3.42 (s)	CH_2 stretching
	3.51 (s)	CH_2 stretching
	5.77 (s)	C = O stretching
	6.85 (m)	CH_2 or CH_3 bending
	7.05 (w)	unidentified
	7.28, 7.40 (w)	CH_2 or CH_3 vibration
	8.41, 8.52 (m)	unidentified
L1	3.42 (s)	CH_2 stretching
	3.51 (s)	CH_2 stretching
	5.78 (s)	C = O stretching
	6.87 (m)	CH_2 or CH_3 bending
	7.05 (w)	unidentified
	7.28, 7.40 (w)	CH_2 or CH_3 vibration
	8.5 (m)	unidentified
L2	2.40 (w)	? water
	2.90 (w)	? water
	3.41 (s)	CH_2 stretching
	3.49 (s)	CH_2 stretching
	5.78 (s)	C = O stretching (aryl ester)
	6.85 (s)	C = C stretching of benzene ring
	7.07 (s)	C = C CH bending
	7.25 (s)	CH_2 or CH_3 vibration
	8.0 -8.7 (s)	C - O - stretching (higher esters)
L3	3.41 (s)	CH_2 stretching
	3.50 (s)	CH_2 stretching
	5.77 (s)	C = O stretching (aryl ester)
	6.85 (m)	C = C stretching of benzene ring
	7.05 (w)	C = C CH bending
	7.25-7.40 (m)	CH_2 or CH_3 vibration
	8.15 (s)	unidentified
	8.50 (s)	C - O - stretching (higher esters)
	8.75 (s)	C - O stretching (esters of aromatic acids)

Table VII (cont'd)

Film	Wavelength of absorption maxima	Probable function grouping
L3 (cont'd)	9.40 (m)	? benzene ring substitution
	9.60 (m)	unidentified
	9.92 (s)	unidentified
	10.27 (m)	? benzene ring substitution
L4* nujol	5.78 (w)	C = O stretching (aryl ester)
	5.85 (w)	C = O stretching (aryl ester)
	6.08 (m-s)	unidentified
	7.79-7.90 (w)	C - O stretching (ester of aromatic acid)
	8.91 (w)	C - H in plane deformation (disubstituted benzene)
	13.91 (w)	unidentified
L5	3.42 (s)	CH_2 stretching
	3.51 (s)	CH_2 stretching
	5.78 (s)	C = O stretching
	6.69 (m)	unidentified
	6.84 (w)	CH_2 or CH_3 bending
	7.05 (w)	unidentified
	7.22-7.38 (w)	unidentified
	8.39-8.52 (m)	unidentified
L6	3.41 (w)	CH_2 stretching
	3.49 (w)	CH_2 stretching
	5.77 (w)	C = O stretching
	6.85 (w)	CH_2 or CH_3 bending
	10.75	unidentified

*(w) - weak
(m) - medium
(s) - strong
} refer to relative absorption intensities for each sample

Table VIII

Results of Extraction with Distilled Water of Heat-Sealed Materials for 2 Hours at Maximum Use Temperature

Film	Extraction temperature (°F)	Sealing conditions		Extractables (mg/in^2)		ppm in solvent at 2.5 ml/in^2
		Temperature (°F)	Swell time (seconds)	Average	Range	
L1	212	250	4	.0222	±.0000	8.88
L2	267	380	7	.0958	±.0062	38.3
L3	276	380	7	.0713	±.0183	28.5
L4	267	400	4	.0631	±.0029	25.2
L5	212	225	4	.0154	±.0004	6.27
L6	289	420	7	.0627	±.0018	25.2

Table IX

Results of Extraction with 0.4% Acetic Acid Solution of Heat-Sealed Materials for 2 Hours at Maximum Use Temperature

Film	Extraction temperature (°F)	Sealing conditions		Extraction (mg/in^2)		ppm in solvent at 2.5 ml/in^2
		Temperature (°F)	Swell time (seconds)	Average	Range	
L1	212	250	4	0.0520	.0093	28.0
L2	267	380	7	0.0713	.0068	28.5
				ave. of 3 runs		
L4	267	400	4	0.0872	.0094	34.8
L5	212	225	4	0.0535	.0036	21.4
L6	289	420	7	0.0430	.0062	17.2
				ave. of 2 runs		

Table X

Results of Extraction with n-Heptane of Heat-Sealed Materials for 2 Hours at 150°F

Film	Sealing conditions: Temperature (°F)	Sealing conditions: Swell time (seconds)	Extractables (mg/in^2): Average	Extractables (mg/in^2): Range	ppm in solvent at 2.5 ml/in^2	Corrected values*: Extractive	Corrected values*: ppm
L1	250	4	.4240	±.0138	.2380	.0848	47.7
L2	380	7	7.110	±.2475	4000	1.420	800
L3	380	7	6.490	±.2775	3630	1.300	726
L4	400	4	.8975	±.0318	502.0	.1790	100
L5	225	4	.2080	±.0170	116.0	.0416	23.2
L6	420	7	.4245	±.0383	240.0	.0848	48.0

*As presented in amendment published in Federal Register, February 10, 1962: 27F.R., 1252, Paragraph 121.2514, Section e, Subparagraph 5.

Table XI

F.D.A. Acceptability

Material	Thickness	Temperature of extraction (°F)	Water		Acetic acid		n-Heptane	
			1	2	1	2	1	2
U1	1	292	+	+	+	+	+	+
U2	1	276	+	+	+	+	+	-
U3	.5	292	+	+	+	+	+	+
U4	1	292	+	+	+	+	+	+
U5	2.5	276	+	+	+	+	-	-
U6	?	212	+	+	+	+	+	-
U7	2	212	+	+	+	+	+	+
L1	2	212	+	+	+	+**	+	+
L2	3	267	+	+	+	+**	-	-
L3	3	276	+	+	+	+**	-	-
L4	2	267	+	+	+	+**	+	-
L5	2	212	+	+	+	+**	+	+
L6	2	289	+	+	+	+**	+	+

1 - Judged on basis of mg extractives/in^2

2 - Judged on basis of ppm at 2 ml/in^2

\+ - Acceptable under present F.D.A. regulations

**Judged on basis of ppm at 2.5 ml/in^2

Table XII

F.D.A. Acceptability - Heat-Sealed Materials

Material	Thickness	Temperature of extraction (°F)	Water		Acetic acid		n-Heptane	
			1	2	1	2	1	2
L1	2	212	+	+	+	+	+	+
L2	3	267	+	+	+	+	-	-
L3	3	276	+	+			-	-
L4	2	267	+	+	+	+	+	-
L5	2	212	+	+	+	+	+	+
L6	2	289	+	+	+	+	+	+

1 - Judged on basis of mg extractives/in^2

2 - Judged on basis of ppm at 2.5 ml/in^2

+ - Acceptable under present F.D.A. regulations

Table XIII

Results of Extraction with Vegetable Oil - Gravimetric Difference Method

Film	I Heptane extractables 2 successive runs 2 hours at 150°F (mg/in^2)	II Cold heptane wash (virgin film) (mg/in^2)	III Heptane extractables following oil extraction and heptane wash (mg/in^2)	IV Oil extractables I - (II + III) (mg/in^2)
L6	.43	.041	.24	.15
L2	6.7	.24	.27	6.2
L3	6.5	.5	.63	5.4
L4	1.0	.016	.55	.43

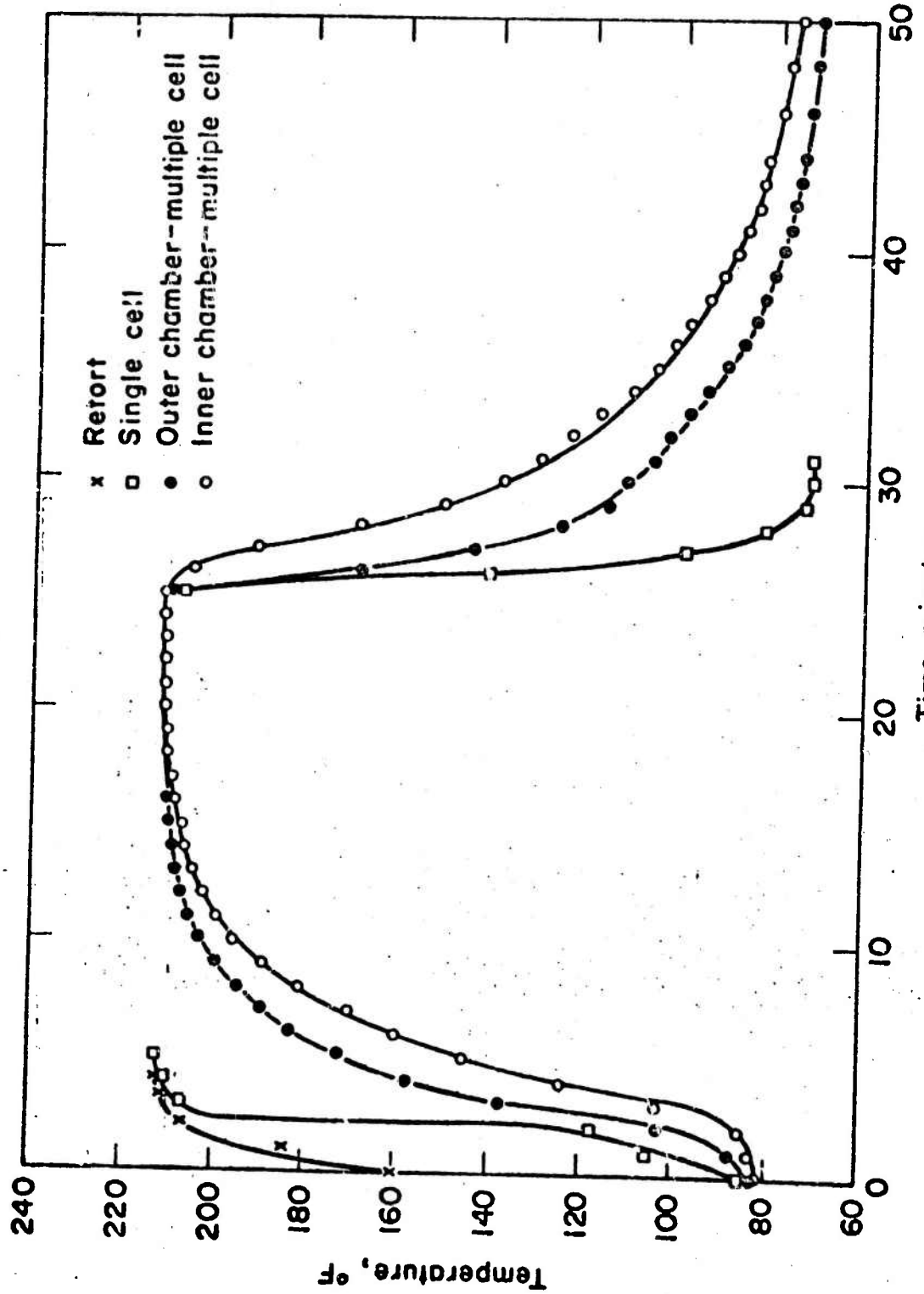

FIGURE 1 HEATING AND COOLING CURVES FOR ASTM CELLS: ROOM TEMPERATURE TO 212°F

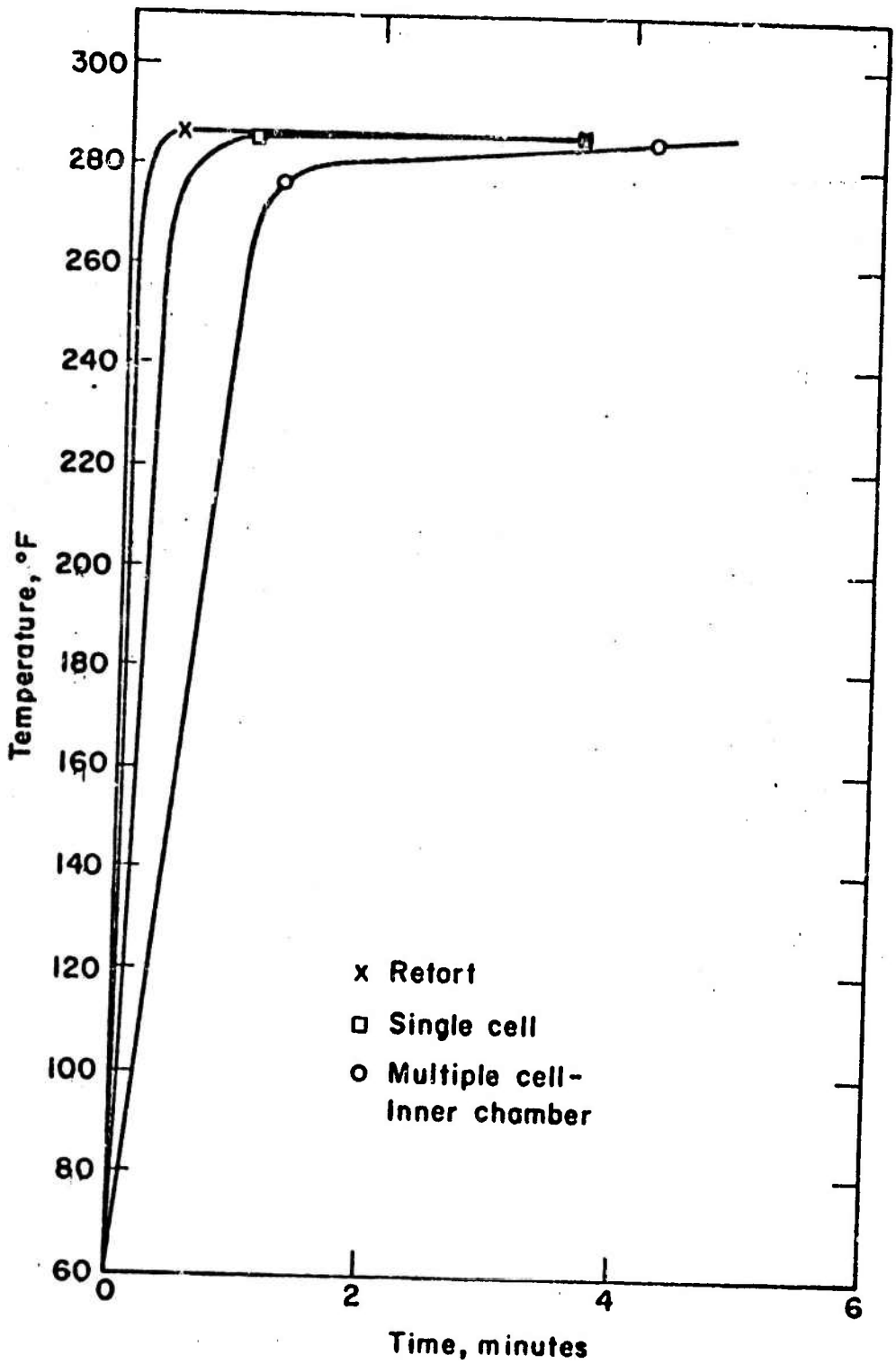

FIGURE 2 HEATING CURVES FOR ASTM CELLS: ROOM TEMPERATURE TO 290°F

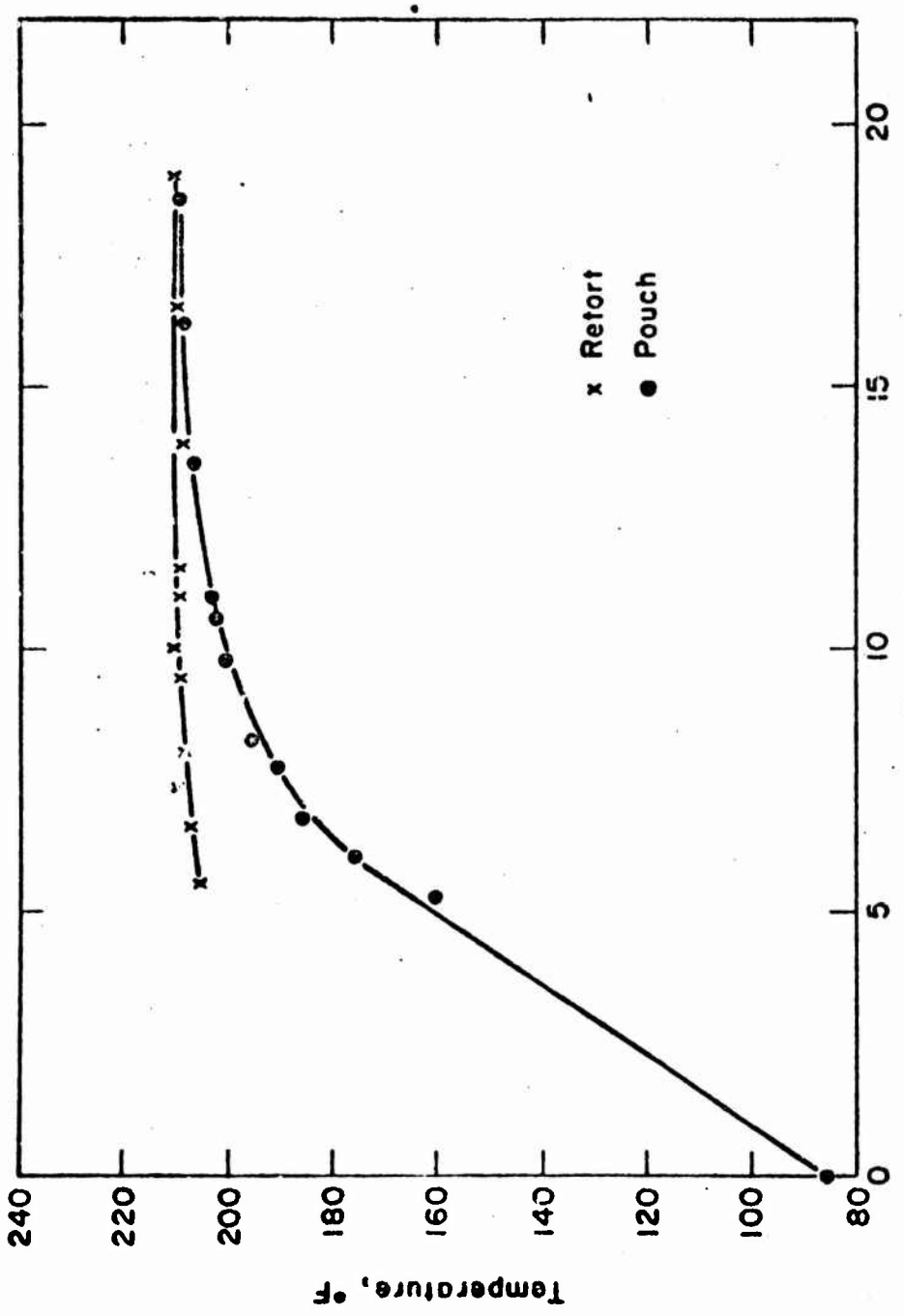

FIGURE 3 HEATING CURVE FOR LAMINATE POUCHES PROCESSED IN WATER-FILLED, SEALED CANS: ROOM TEMPERATURE TO 212°F

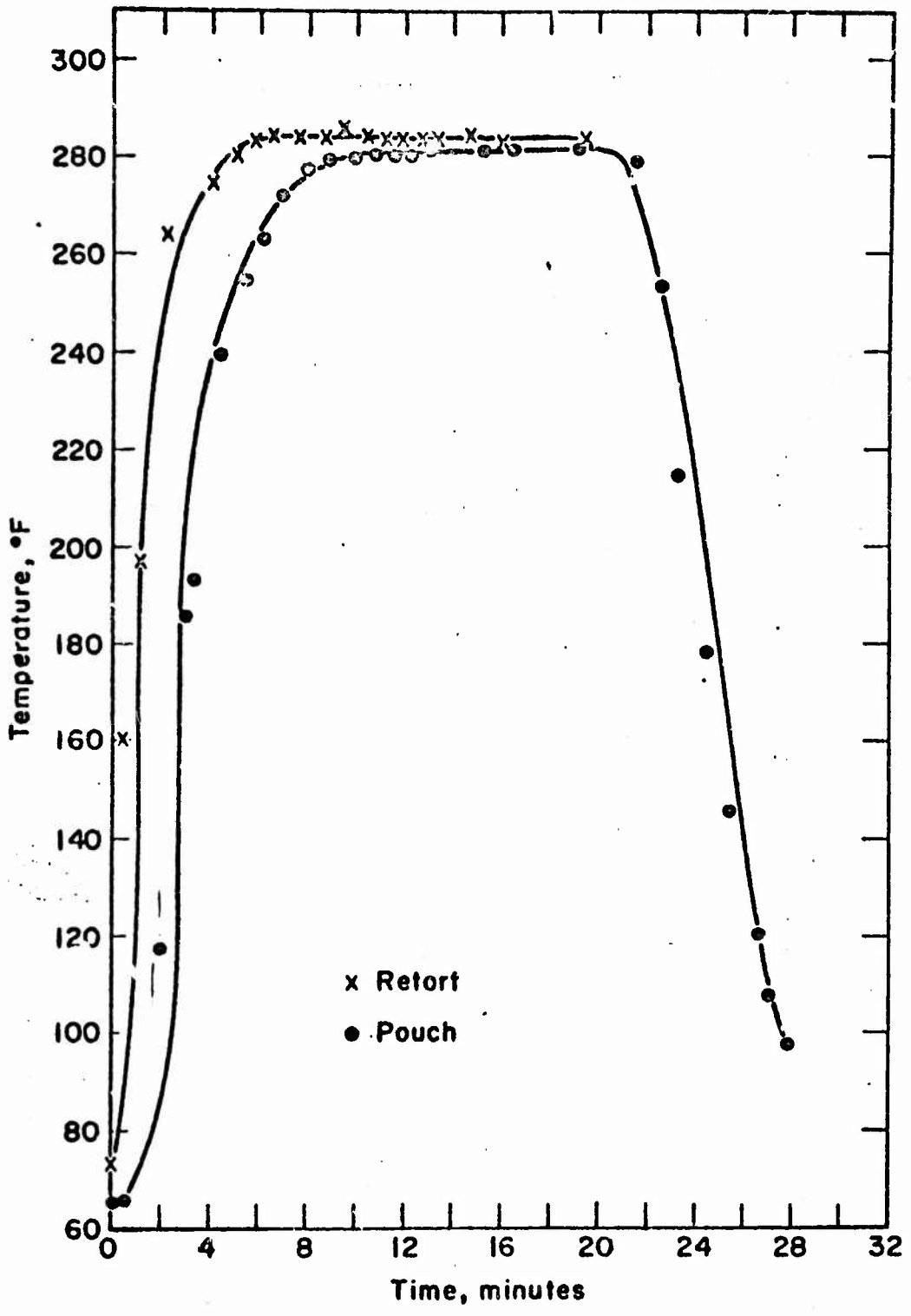

FIGURE 4 HEATING AND COOLING CURVES FOR LAMINATE POUCHES PROCESSED IN WATER FILLED, SEALED CANS: ROOM TEMPERATURE TO 290°F

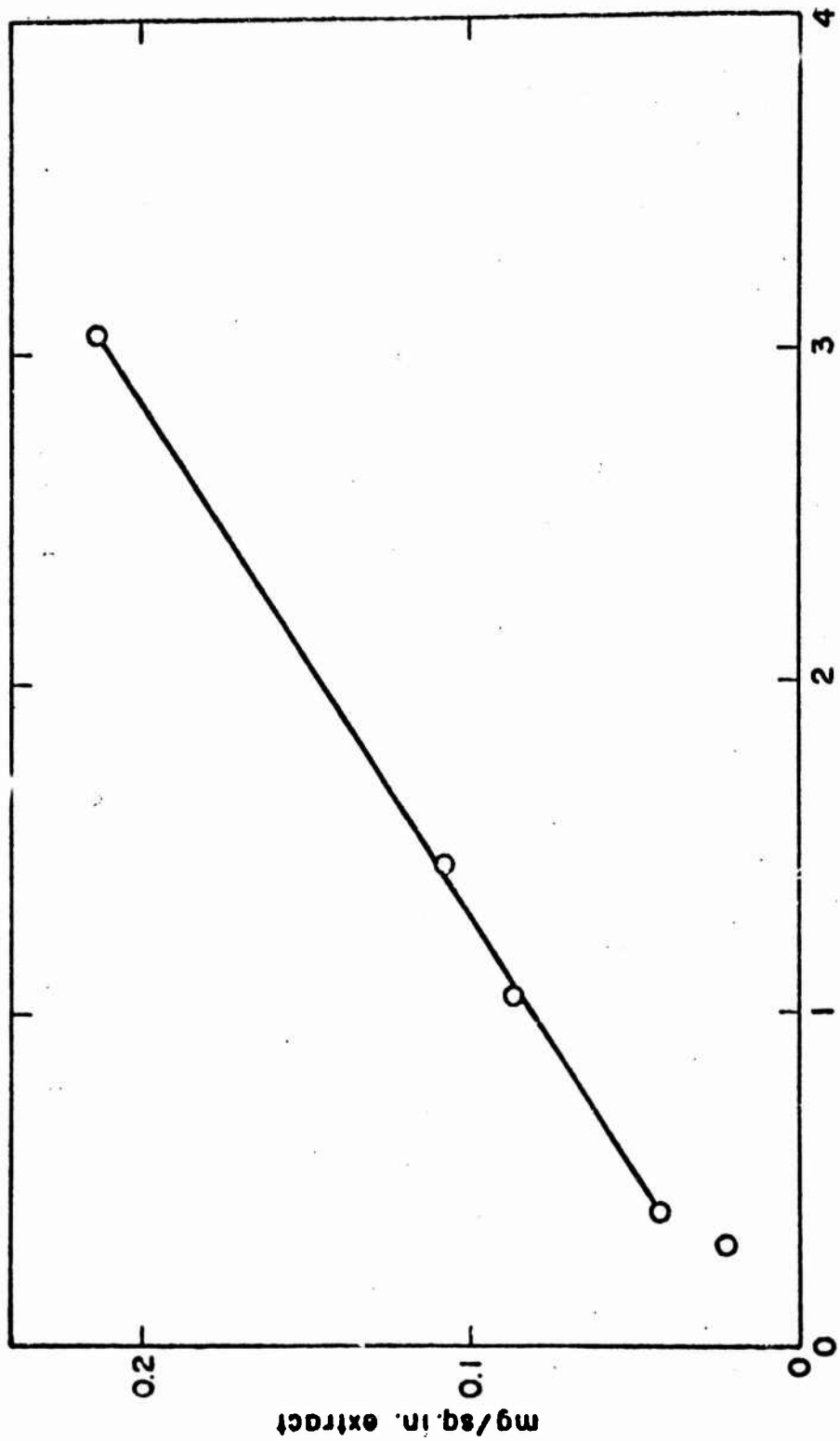

FIGURE 3 NEPHELOMETRIC STANDARD CURVE FOR L-6

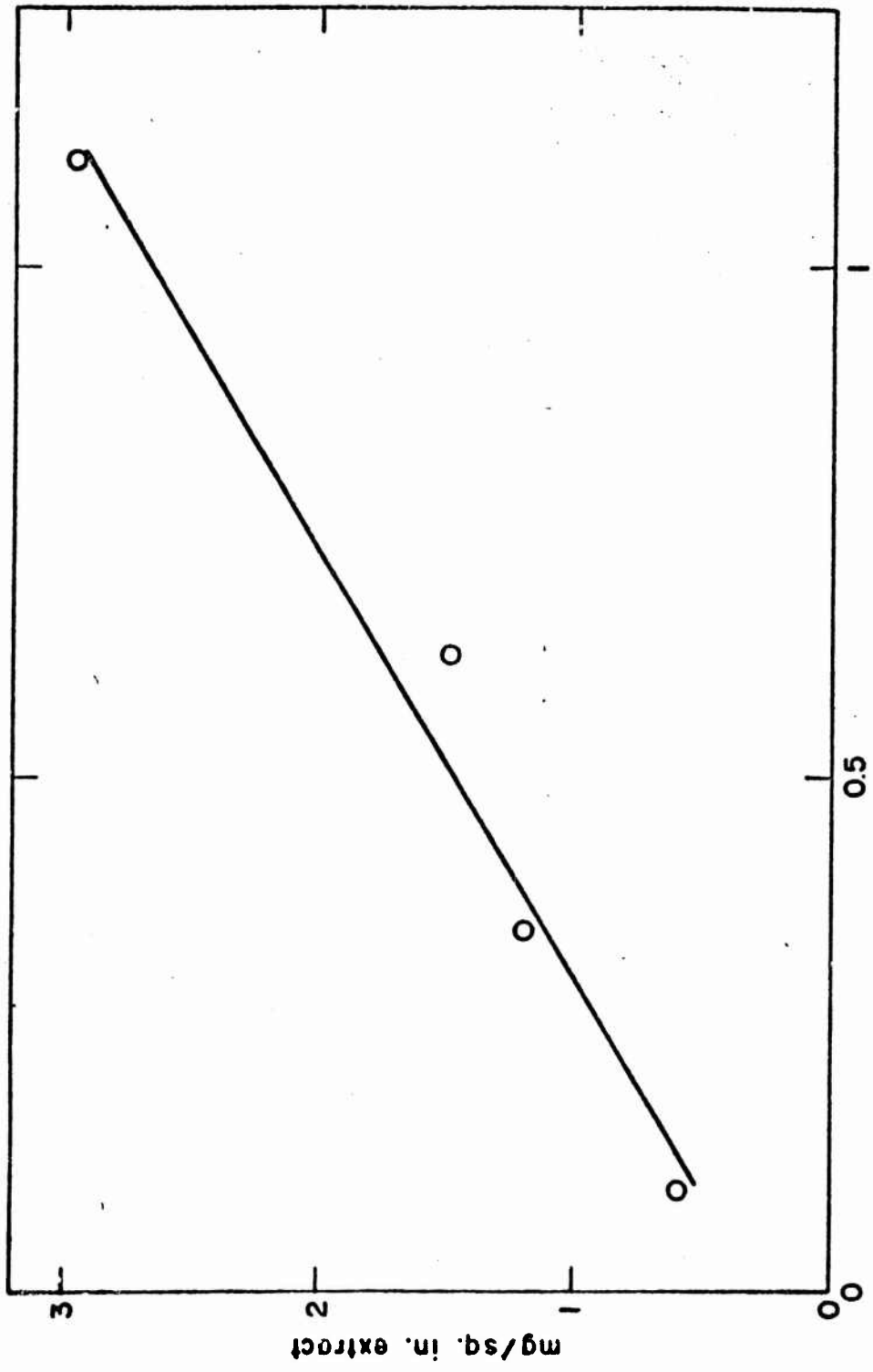

FIGURE 6 NEPHELOMETRIC STANDARD CURVE FOR L-1